



Review article

The precautionary principle and chemicals management: The example of perfluoroalkyl acids in groundwater



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ABSTRACT

Already in the late 1990s microgram-per-liter levels of perfluorooctane sulfonate (PFOS) were measured in water samples from areas where fire-fighting foams were used or spilled. Despite these early warnings, the problems of groundwater, and thus drinking water, contaminated with perfluoroalkyl and polyfluoroalkyl substances (PFASs) including PFOS are only beginning to be addressed. It is clear that this PFAS contamination is poorly reversible and that the societal costs of clean-up will be high. This inability to reverse exposure in a reasonable timeframe is a major motivation for application of the precautionary principle in chemicals management. We conclude that exposure can be poorly reversible; 1) due to slow elimination kinetics in organisms, or 2) due to poorly reversible environmental contamination that leads to continuous exposure. In the second case, which is relevant for contaminated groundwater, the reversibility of exposure is not related to the magnitude of a chemical's bioaccumulation potential. We argue therefore that all PFASs entering groundwater, irrespective of their perfluoroalkyl chain length and bioaccumulation potential, will result in poorly reversible exposures and risks as well as further clean-up costs for society. To protect groundwater resources for future generations, society should consider a precautionary approach to chemicals management and prevent the use and release of highly persistent and mobile chemicals such as PFASs.

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1. Introduction

Perfluoroalkyl and polyfluoroalkyl substances (PFASs), most notably perfluoroalkyl acids (PFAAs) such as perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are present at elevated concentrations in surface waters, soils, groundwater and drinking water near to

domestic and military airports, oil and gas sites, and firefighter training areas at multiple locations globally (for examples, see Table 1) (Awad et al., 2011; Moody et al., 2002; Kwadijk et al., 2014; De Solla et al., 2012; Filipovic et al., 2015; Kärrman et al., 2011; Moody et al., 2003; Schultz et al., 2004a; McGuire et al., 2014; Backe et al., 2013; Weiß et al., 2012; Rumsby et al., 2009; Järnberg et al., 2001). The contamination of the environmental media and drinking water by PFASs at these multiple global sites mostly originates from the repeated use and uncontrolled release of fire-fighting foams containing PFASs to the environment during fire-fighting and firefighter training activities over

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Table 1

Measured concentrations of selected examples of PFASs in the environmental media at sites where fire-fighting foams have been used or spilled. LOD = limit of detection.

Sampling sites	PFOA	PFOS	PFHxS	Ref.
<i>Surface water (ng/L)</i>				
Toronto Pearson Airport, Canada		29–690		Awad et al. (2011)
Toronto Pearson Airport, Canada	<LOD–11,300	<LOD–995,000	<LOD–134,000	Moody et al. (2002)
Schiphol Airport, The Netherlands		20–490		Kwadijk et al. (2014)
Hamilton International Airport, Canada	7.4–62.4	7–458		De Solla et al. (2012)
Air force base F18, Sweden	<1–8.8	<1–45.8	<0.5–25.1	Filipovic et al. (2015)
Flesland airport, Norway		1427–2078		Kärman et al. (2011)
<i>Groundwater (ng/L)</i>				
Wurtsmith Air Force Base, USA	<LOD–105,000	4000–110,000	9000–120,000	Moody et al. (2003)
Tyndall Air Force Base, USA	<LOD–116,000	147,000–2,300,000	107,000–920,000	Schultz et al. (2004a)
Fallon Naval Air station, USA	<LOD–6570	<LOD–380,000	<LOD–876,000	Schultz et al. (2004a)
Ellsworth Air Force Base, USA	400–300,000	5000–75,000		McGuire et al. (2014)
US military base, USA	12,000–220,000	15,000–78,000	36,000–360,000	Backe et al. (2013)
US military base, USA	8.6–57,000	88–65,000	81–1700	Backe et al. (2013)
Fire training area Cologne, Germany	<LOD–160	20–8350	<10–2360	Weiß et al. (2012)
Air force base F18, Sweden	<1–4470	<1–42,200	<0.5–3470	Filipovic et al. (2015)
Jersey Airport, UK		10,000–98,000		Rumsby et al. (2009)
<i>Soil (ng/g dw)</i>				
Ellsworth Air Force Base, USA	10–10,500	10–34,000		McGuire et al. (2014)
Air force base F18, Sweden		5–8300		Filipovic et al. (2015)
Flesland airport, Norway		<LOD–1905		Kärman et al. (2011)
<i>Sediment (ng/g dw)</i>				
Toronto Pearson Airport, Canada		1–13		Awad et al. (2011)
Schiphol Airport, The Netherlands		0.5–14		Kwadijk et al. (2014)

many years. Since the mid-1960s (see timeline in Fig. 1) a complex mixture of PFASs (including a wide range of PFAAs and their precursors derived from perfluoroalkane sulfonyl fluorides (PASFs) or fluorotelomer raw materials) were or have been added as; (1) film formers in aqueous

film-forming foams (AFFFs) and film-forming fluoroproteins (FFFPs), (2) as fuel repellents in fluoroprotein foams, and (3) as foam stabilizers in FFFPs and alcohol-resistant AFFFs (McGuire et al., 2014; Backe et al., 2013; Moody and Field, 2000; Prevedourous et al., 2006; Moe et al.,

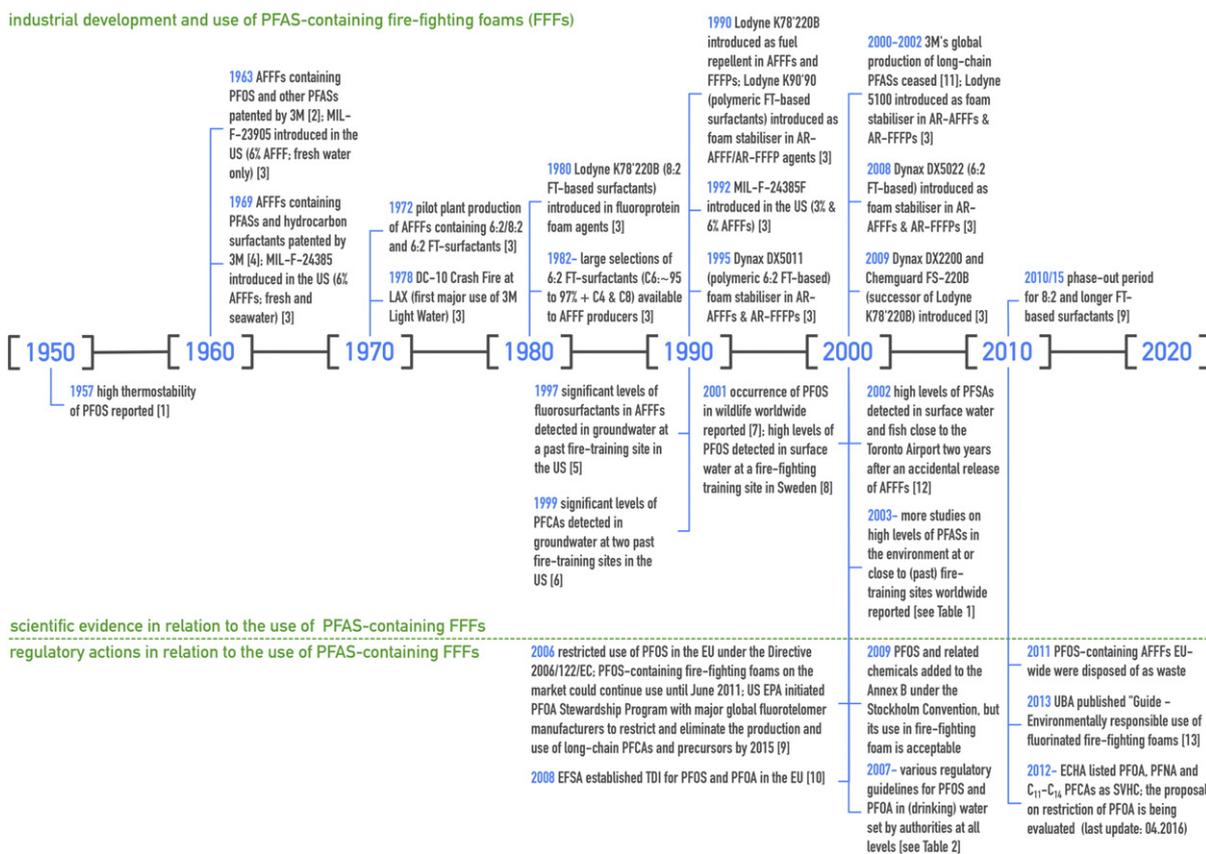


Fig. 1. Timeline of industrial development, scientific evidence and regulatory actions in relation to the use of PFAS-containing fire-fighting foams. References: [1] Gramstad and Haszeldine (1957); [2] Tuve and Jablonski (1966); [3] Kleiner and Jho (2009); [4] Francen (1969); [5] Levine et al. (1997); [6] Moody and Field (1999); [7] Giesy and Kannan (2001); [8] Järnberg et al. (2001); [9] US EPA (2006); [10] EFSA (2008); [11] 3M (2000); [12] Moody et al. (2002); [13] UBA (2013).

2012; Guelfo and Higgins, 2013; Wang et al., 2013; D'Agostino and Mabury, 2014).

Given that elevated concentrations of PFAAs are detected in groundwater at multiple locations, groundwater is often the primary source of drinking water, and certain PFAAs (e.g. PFOA and PFOS) have been associated with severe toxic effects (De Wit, 2015), public concerns have arisen in recent years with respect to the risks from human exposure to PFAAs via drinking water. For example, the drinking water works in the municipality of Kallinge, Sweden were immediately closed down after contamination of the groundwater was discovered near a Swedish Air Force base where AFFFs have been used (Jakobsson et al., 2014). At that time, in December 2013, drinking water levels of PFOS in the outgoing water at a drinking water treatment plant in Kallinge were determined to be between 800 and 10,000 ng/L ($n = 3$) (Jakobsson et al., 2014). The same study also found that the human serum levels of some PFAAs in the population of Kallinge (e.g. median serum levels of 290 ng/mL PFOS) were approximately 30 times higher than the background exposed population of Sweden (Jakobsson et al., 2014; Glynn et al., 2012). In response to the rising public concern, guideline values for PFAAs in drinking water have been set in many countries to protect against this undesired human exposure pathway. However, determination of guidelines or drinking water standards is not straightforward due to complex toxicokinetics and -dynamics of PFAAs as well as the paucity of conclusive epidemiological evidence (Frisbee et al., 2010; Steenland et al., 2010). A precautionary approach is therefore often used in setting the guidelines i.e., an approach which takes into account that some information may be missing. Depending on the premises and assumptions being used (e.g. chronic or short-term exposure to the contaminated drinking water), risk assessments (EFSA, 2007; Borg et al., 2013) have led to different conclusions regarding safe drinking and natural water levels across countries (see Table 2 for a summary).

In addition to the challenge of defining guideline values, there are technical challenges to reverse the environmental and human exposure to PFASs. PFAAs are not removed from drinking water by conventional treatment technologies (Thompson et al., 2011; Eschauzier et al., 2012). Advanced technologies based on granular activated carbon (GAC) filters (Lampert et al., 2007; Yu et al., 2009), reverse osmosis (Tang et al., 2006), nanofiltration (Tang et al., 2007), ion exchange (Yu et al., 2009) or sorption using modified biopolymers (Yu et al., 2008) have been studied to remove PFAAs from contaminated water. Among

them, GAC filtration has been the most widely applied technology due to its cost-efficiency and effectiveness in removing PFOS and PFOA from drinking water (Skutlarek et al., 2006; Bartell et al., 2010; Brede et al., 2010). However, the performance of the technologies mentioned above decreases with decreasing perfluoroalkyl chain length to the point that the technologies no longer function. For example, perfluorobutanoic acid (PFBA) and perfluorobutane sulfonate (PFBS) cannot be removed by GAC (Eschauzier et al., 2012; Lampert et al., 2007; Yu et al., 2009; Tang et al., 2006). Additionally, these technologies require costly disposal of the highly contaminated concentrates or sorbent materials, usually by high-temperature incineration. Furthermore, the PFAS removal technologies mentioned above only represent measures to reduce human exposure via drinking water. Complete remediation of AFFF-contaminated sites is a much more challenging task, both technically and financially, that may require excavation of contaminated soil, pumping and treating of groundwater or in-situ methods to remove contaminants from soil and aquifers (Oliaei et al., 2013). Inadequate remediation measures have been shown to be counterproductive by increasing the mobility of PFASs or advancing the transformation of precursor compounds to PFAAs (McGuire et al., 2014).

Fire-fighting foams have long been known to be a source of PFAAs to the environment. High levels of PFAAs were reported in groundwater impacted by fire-fighting activities in 1999 (Moody and Field, 1999) and following a spill of AFFFs in a creek in Toronto, Canada in 2002 (Moody et al., 2002). However, despite these early warnings, the problems associated with AFFF-contamination are only beginning to be addressed. Reasons for delays in actions on PFAA contamination include: (1) time needed for analytical chemists to develop proper analytical methods and measure the geographical extent and seriousness of the AFFF-related contamination problem, (2) time needed for researchers to fill data gaps on relevant hazardous properties (e.g. toxicity), (3) time needed to properly review available data before setting regulatory guidelines and making decisions, and (4) time needed to devise, agree on and implement regulatory and management measures. Fig. 1 provides a timeline of key industrial and regulatory events related to production, supply, use and management of PFAS-containing fire-fighting foams. Briefly, production of PFAS-containing AFFFs began in the early 1960s, environmental contamination problems were discovered about 40 years later, and the issue began to be systematically addressed another 10–15 years later.

Table 2

Regulatory guidelines for PFOA and PFOS (ng/L) in drinking water set by provincial and national authorities.

	PFOA	PFOS	Ref.
German Drinking Water Commission (HPV ₁)	100 ^{a,c}	100 ^{a,c}	German DWC (2011)
German Drinking Water Commission (GV)	300 ^{a,d}	300 ^{a,d}	German DWC (2011)
German Drinking Water Commission (PAV _i)	500 ^{a,e}	500 ^{a,e}	German DWC (2011)
German Drinking Water Commission (PAV _o)	5000 ^{a,c}	5000 ^{a,f}	German DWC (2011)
Danish Environmental Protection Agency	100 ^b	100 ^b	DEPA (2015)
National Food Agency, Sweden	90 ^b	90 ^b	NFA (2013)
UK Drinking Water Inspectorate (tier 1)	300	300 ^g	DWI (2007)
UK Drinking Water Inspectorate (tier 2)	10,000	1000 ^h	DWI (2007)
UK Drinking Water Inspectorate (tier 3)	90,000	9000 ⁱ	DWI (2007)
New Jersey Department of Environmental Protection, USA	40	–	NJ DEP (2007)
Minnesota Department of Health, USA	300	300	MDH (2008)
North Carolina Secretary's Science Advisory Board on Toxic Air Pollutants, USA	1000	–	NC SAB (2010)
Maine Center for Disease Control & Prevention, USA	100	–	MCDCP (2014)
US EPA Office of Water	400 ^j	200 ^j	US EPA (2012)

^a Refers to the sum of PFOA and PFOS present in drinking water.

^b Refers to the sum of PFASs including PFOA and PFOS (the sum of 7 PFASs in Sweden and the sum of 12 PFASs in Denmark) present in drinking water.

^c Health-based precautionary value (long-term minimum quality goal) for non-genotoxic substances.

^d Strictly health-based guidance value for safe lifelong exposure for all population groups.

^e Precautionary action value for infants.

^f Precautionary action value for adults.

^g Minimum action to be taken: consult with local health professionals; and monitor levels in drinking water.

^h Minimum action to be taken: as tier 1 plus: put in place measures to reduce concentrations to below 1000 ng/L (PFOS) or 10,000 ng/L (PFOA) as soon as practicable.

ⁱ Minimum action to be taken: as tier 2 plus: ensure consultation with local health professionals takes place as soon as possible; and take action to reduce exposure from drinking water within 7 days.

^j Provisional short-term value.

In this paper we consider how application of the precautionary principle (i.e. introduction of a novel “reversibility of exposure”-based chemicals management paradigm) at an earlier stage might have led to earlier and more effective regulatory and management actions on PFASs. In recent years, fluorinated alternatives have come on the market to replace the legacy long-chain PFASs in certain applications. Among others, AFFFs based principally (>99%) on 6:2-fluorotelomer raw materials (e.g. 6:2-fluorotelomer sulfonamide alkylbetaine in Forafac® 1157 and 6:2-fluorotelomer sulfonamide aminoxide in Forafac® 1183) have been commercialized to replace long-chain PFASs-containing AFFFs (Wang et al., 2013). We also apply the proposed “reversibility of exposure”-based chemicals management paradigm to these fluorinated alternatives currently used in AFFFs.

2. Background to the precautionary principle

One commonly accepted definition of the precautionary principle is provided in Principle 15 of the Rio Declaration on Environment and Development as follows: “Where there are threats of serious or irreversible damage, lack of full scientific certainty shall not be used as a reason for postponing cost-effective measures to prevent environmental degradation” (UNEP, 1992). The precautionary principle has emerged as an approach in environmental regulation (Maguire and Ellis, 2005). In the context of chemicals management, it has been argued in the literature for about 40 years that prioritization of the precautionary decision-making process should be governed by the persistence of a chemical (Stephenson, 1977; Klöpffer, 1994; Scheringer, 1997; Webster et al., 1998; Gouin, 2010; Persson et al., 2013). In practice, persistence is adopted as a key criterion for listing chemicals under the Stockholm Convention on Persistent Organic Pollutants, a global treaty that is guided by the precautionary principle (UNEP, 2001). This idea can also be found in the European chemicals regulation, REACH, in which the PBT (persistent, bioaccumulative and toxic) and vPvB (very persistent, very bioaccumulative) designations are cornerstones of classification tools to regulate chemicals based on the precautionary principle (REACH, 2007). The regulation of PBT and vPvB chemicals is motivated as follows: “What distinguishes the PBT and vPvB substances from other substances is that ... consequences of an underestimation of adverse effects are not easily reversible by regulatory action, i.e. the effect is occurring or is likely to occur at a certain point in time and, even if there is immediate regulatory action to prevent further emission, the adverse effects will continue” (ECHA, 2012). The central message here is that the target of regulatory actions is a rapid reduction in effects, as otherwise society may face a problem that cannot be managed. Assuming that adverse effects are still mitigatable by reducing exposure, the successful achievement of this target relies on the reversibility of exposure, i.e. that the exposure to a chemical can be rapidly reduced once the emissions are controlled. Hence, it is postulated that reversibility of exposure is a central concept that should guide the incorporation of the precautionary principle in chemicals management.

Recently, another type of hazard assessment scheme was developed to identify chemicals that are planetary-boundary threats (Persson et al., 2013; Rockström et al., 2009), which are chemical-related problems that could destabilize the Earth system. Poorly reversible exposure was considered as one of the three characteristics that a chemical must possess to be considered as a planetary-boundary threat (Persson et al., 2013). In this previous work, it was noted that the well-established hazard assessment indicators (P, B and long-range transport potential (L RTP)) can provide some useful information on reversibility of exposure, but they do not generally address all aspects (e.g. the reversibility and spatial distribution of emissions is not addressed with P, B and L RTP), so new methodologies are required.

The following sections explore how reversibility of exposure can be assessed using PFAS contamination of groundwater as a case study. The chemicals regulation which most closely approaches reversibility of exposure is the vPvB designation in REACH, which stipulates that if both a

persistence and a bioaccumulation criterion are exceeded then the chemical is considered a hazard (i.e., vPvB) (ECHA, 2012). The vPvB criteria are applied to PFASs, which have been or are currently used in fire-fighting foams. It is further discussed if vPvB provides a good measure of poorly reversible exposure.

3. How does the persistence criterion relate to the reversibility of exposure?

To assess the possible hazard of environmental exposure to chemicals, environmental persistence is frequently used as an indicator describing the duration of exposure. Environmental persistence can be expressed by either a half-life or residence time of a chemical in the environment (Klöpffer, 1994; Webster et al., 1998). Although a simple concept to understand, estimating persistence for a given chemical turns out to be a challenging task because of the difficulty in measuring and estimating degradation half-lives for chemicals (Klöpffer, 1994; Webster et al., 1998; MacLeod and McKone, 2004; Müller-Herold, 1996; Stroebe et al., 2004; Wegmann et al., 2009). Under REACH, a chemical is considered to have violated the environmental persistence criterion if its degradation half-life ($t_{1/2, \text{DEC}}$) in marine, fresh or estuarine water is >40 days (or >60 days for vP) or if its half-life in marine, fresh or estuarine sediment is >120 days (>180 days for vP) or if its half-life in soil is >120 days (>180 days for vP). Additionally, the persistence of relevant transformation/degradation products should also be taken into account; this is particularly relevant for PFASs because, although some PFASs (i.e. the so-called precursors) are degradable, they ultimately degrade into highly stable end products (often PFAAs) due to the high stability of perfluoroalkyl chains (Scheringer et al., 2014; Schultz et al., 2004b). For PFASs, an alternative measure of persistence e.g. “joint persistence” is thus more appropriate for assessing environmental persistence. “Joint persistence” quantifies the environmental persistence of a parent compound and a selection of relevant transformation products (Fenner et al., 2000). Because PFASs are, or ultimately degrade to, stable end products, all PFASs possess a joint persistence that exceeds all three of the REACH single-media persistence criteria mentioned above.

It is now worth considering how the single-media persistence criteria relate to the reversibility of exposure in groundwater. The hydraulic residence time of groundwater at a site sets a minimum limit on the residence time of water-soluble PFASs because transport away from the site in water is the only removal mechanism. If PFASs sorb to solids in the soil or aquifer material, the transport of PFASs will be retarded and their residence time will be even longer than the residence time of the groundwater. Given the long residence times of most groundwaters (Maloszewski and Zuber, 1982; McGuire et al., 2005; Goody et al., 2006), the residence times of PFASs in groundwater will nearly always be >40 days and can be of the order of millennia. Thus, PFAS-contaminated groundwater can act as a long-lasting source, leading to poorly reversible exposure to PFASs in the subterranean environment as well as where the contaminated groundwater resurfaces.

Exposure to PFASs may appear to be reversible in the short term in some parts of the environment, as levels of PFOS, PFOA and some other PFAAs are reported to be declining in some regions (Armitage et al., 2006; Armitage et al., 2009; Cousins et al., 2011; Johansson et al., 2014). However, this decline is not due to chemical degradation, but due to the distribution from source regions to the entire global environment via advection, dispersion, dilution and burial processes (Prevedouros et al., 2006; Armitage et al., 2006; Armitage et al., 2009). Modelling studies have shown that recent declines in PFAA concentrations in the Northern Hemisphere are due only to transport processes and that oceans are the ultimate reservoir for PFAAs (Armitage et al., 2006; Armitage et al., 2009). Ocean levels of PFAAs will decline very slowly because the only removal process for PFAAs in surface oceans is the slow mixing into the deep oceans on the hundred-year scale (Armitage et al., 2006; Armitage et al., 2009).

4. How does the bioaccumulation criterion relate to poorly reversible exposure?

Bioaccumulation is a criterion for hazard assessment in a range of chemicals regulations including the Stockholm Convention, UNECE Convention on Long-range Transboundary Air Pollution (CLRTAP), and REACH (Webster et al., 1998; UNEP, 2001; UNECE, 1979). Under REACH, bioaccumulation is primarily evaluated on the basis of the chemical's bioconcentration factor in aquatic species (usually fish; BCF_{FISH}), and the chemical is considered to have violated the "bioaccumulation" (B) criterion if BCF_{FISH} exceeds 2000 and the "very bioaccumulative" (vB) criterion if the BCF_{FISH} exceeds 5000. As of recently, it is also possible to consider terrestrial bioaccumulation, bioaccumulation in human tissues, and evidence from field studies (e.g. food web biomagnification studies) in a weight-of-evidence approach when assessing bioaccumulation (Gobas et al., 2009; ECHA, 2014). Below we query if these bioaccumulation criteria are related to the reversibility of exposure.

In doing so, we need to differentiate between external and internal exposure because bioaccumulation "translates" external exposure to the corresponding internal exposure. In some cases, the time scales of external and internal exposure are different. When the elimination kinetics in an organism are slow, this affects the reversibility of internal exposure. This occurs when the elimination kinetics in the organism are slower than the kinetics for reduction of external exposure. From the perspective of the persistence criterion in hazard regulation, this becomes interesting when the half-life for elimination from the organism exceeds the regulatory threshold for the half-life of the chemical in the medium that the organism lives in. For instance, if the elimination half-life of a chemical in fish exceeded the single-media persistence threshold for water under REACH ($t_{1/2, DEG} > 40$ days), then the reversibility of the fish's exposure would be > 40 days and thus similar to the reversibility of exposure to persistent chemicals, regardless of whether the chemical in question was persistent in water. Hence, elimination half-life is a bioaccumulation property that can determine the reversibility of internal exposure.

If the primary regulatory criterion for assessing bioaccumulation, BCF_{FISH} , is to be useful for describing the reversibility of internal exposure, then BCF_{FISH} needs to be a good predictor of the elimination rate constant in fish. For small non-polar organic chemicals, there is often a good correlation between the BCF_{FISH} and the elimination rate constant (Gobas and Morrison, 2000; Crookes and Brooke, 2011), which is due to the propensity of these chemicals to partition into the same tissue (lipids) and their relatively constant uptake efficiencies (Gobas and Morrison, 2000; Crookes and Brooke, 2011). However, this correlation breaks down for neutral, polar chemicals for which the uptake efficiency is strongly influenced by the polarity (Armitage et al., 2013). Furthermore, for ionizing compounds, distribution in fish occurs through mechanisms other than partitioning into adipose tissues (e.g., via protein-binding and/or strong partitioning to membrane phospholipids in the case of PFAAs; Armitage et al., 2012; Ng and Hungerbühler, 2014), which results in further complexity and challenges in understanding the correlation between BCF_{FISH} and the elimination rate constants. Despite these potential complications in uptake mechanisms, BCF_{FISH} has been shown to be a good predictor of the elimination rate constant for PFAAs (Martin et al., 2003) and therefore provides an indication of the reversibility of exposure for PFAAs in fish.

A further condition for the usefulness of the regulatory criterion for bioaccumulation is that the BCF_{FISH} predicts (or at least is conservative with respect to) elimination rate constants in higher organisms (e.g., humans). For small non-polar molecules in water-respiring organisms this is generally the case, as the excretion of such a compound is via passive diffusion leading to similarity across species after allometric scaling (Nagilla and Ward, 2004). For chemicals eliminated primarily via metabolism, BCF_{FISH} is often conservative with respect to higher organisms as metabolism is generally more rapid in higher organisms

than in fish (Arnot et al., 2010). However, BCF_{FISH} may not be conservative for higher organisms in food webs where there is significant biomagnification of the chemical arising from dietary exposure. Furthermore, for slowly metabolized chemicals with low air-water partition coefficients, BCF_{FISH} may not be conservative with respect to air-breathing organisms because elimination via respiration of air is slower than elimination via respiration of water (Czub and McLachlan, 2004). For PFAAs, elimination occurs through different mechanisms in aquatic and terrestrial species: In mammalian species it is governed by renal and biliary clearance (Harada et al., 2007; Han et al., 2012), whereas in fish PFAAs can also be eliminated via the respiratory system (i.e. gills). Consequently, elimination is much more efficient in fish than in (some) mammalian species (Han et al., 2012; Ng and Hungerbühler, 2014). For instance, PFOA and PFHxS have low BCF_{FISH} due to rapid elimination (Martin et al., 2003), but both chemicals are only slowly eliminated in humans, with half-lives on the scale of years (Olsen et al., 2007).

In summary, bioaccumulation is not a prerequisite for poor reversibility of internal exposure. Poor reversibility of internal exposure occurs if the chemical is persistent in the environment or if the chemical is slowly eliminated from the organism, even if the chemical is not persistent in the environment. For the hazard assessment of PFAAs, bioaccumulation is generally not relevant because the persistence of PFAAs in the environment is much greater than their residence time in humans and top predators. In situations where external exposure decreases rapidly (e.g., as a result of dilution of PFAA contamination in the environment or of technical measures taken to reduce exposure), low elimination rate constants from the organism may still be the factor limiting the reversibility of internal exposure. In the case of groundwater contamination, however, dilution is low and thus P is the only relevant criterion for determining if poorly reversible exposure will occur.

5. Case study of poor reversibility of human exposure to short-chain PFASs via drinking water

Based on the discussion of P and B above, we argue that AFFFs based on short-chain PFASs will also lead to a poorly reversible exposure even though they are not bioaccumulative according to current regulatory criteria. To illustrate this we considered the dynamics of human serum concentrations from exposure via drinking water to perfluorohexanoic acid (PFHxA) and PFOS respectively. PFHxA was chosen as an example since it is an impurity and ultimate degradation product of 6:2-fluorotelomer-based AFFFs (Wang et al., 2011; Weiner et al., 2013) and has a shorter elimination half-life in humans (14–49 days in highly exposed populations) than PFOS (Russell et al., 2013; Zhou et al., 2014). Given that PFHxA is more water soluble and less sorptive than PFOS, it will be even more mobile in the subsurface environment (Vierke et al., 2013).

Therefore, if 6:2-fluorotelomer-based AFFFs are manufactured, used and released in a similar way and amount to the legacy PFOS-based AFFFs and that they similarly environmentally degrade to form PFAAs, it can be expected that concentrations of PFHxA in nearby surface- and groundwaters will be similarly high as those found for PFOS. Fig. 2 shows the effect of identical drinking water levels in aquifers contaminated with PFOS and PFHxA (groundwater levels shown in Fig. 2b) on the internal human exposure (serum concentrations) to these substances (serum levels shown in Fig. 2a). Details regarding the model simulations are provided in the Supplementary material. Overall, the magnitude of internal human exposure (Fig. 2a) is substantially lower for PFHxA than for PFOS for a human exposed to equal amounts of PFOS and PFHxA via drinking contaminated groundwater over a long period (Fig. 2a). In Scenario 1 it is assumed that emissions to groundwater are stopped after 5 years, but no additional measures are taken to reduce groundwater concentrations. Under these conditions both PFOS and PFHxA decrease slowly in human serum (Fig. 2a) with the reversibility of human exposure being primarily governed by the residence

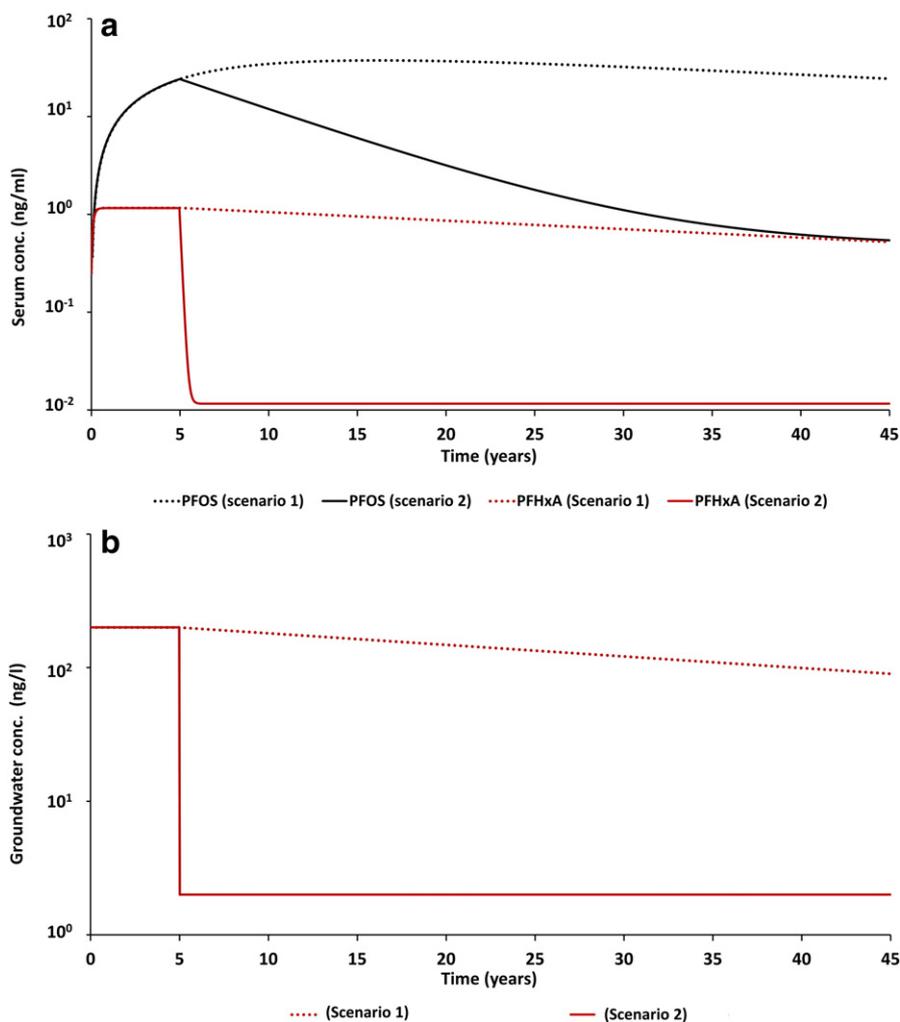


Fig. 2. Predicted human serum concentrations (a) in a population being exposed to PFOS and PFHxA, respectively, from drinking contaminated groundwater (b). The dotted lines represent a scenario where no suitable treatment technology is available and the drinking water concentrations decrease with the residence time of groundwater ($\tau = 50$ years), i.e. Scenario 1. The solid lines illustrate a continuous exposure to water concentrations at 200 ng/L for 5 years before a clean-up technology is installed to remove 99% of the contamination in drinking water, i.e. Scenario 2. Note the logarithmic y-axis.

time of groundwater (Fig. 2b). In Scenario 2 it is assumed that PFAS concentrations in groundwater are effectively reduced by proper measures after emissions ceased. Humans exposed to the contaminated drinking water depicted in Fig. 2a would then be able to eliminate the shorter-chain PFHxA within months, whereas a significant lag-time would be observed for PFOS serum concentrations. Since shorter-chain PFAAs are much more challenging to remove from drinking water than their long-chain analogues (as discussed above), the only technical solution to reduce external exposure to short-chain PFASs (Scenario 2) may be to shift water supply sources. Thus, although the elimination of PFHxA from humans is faster than PFOS, the exposure will be equally poorly reversible until technically and financially feasible exposure mitigation measures are identified and taken.

6. Discussion

In hindsight, many of the worst cases of chemical pollution in recent history were the result of the release of large quantities of persistent chemicals or materials (e.g. polychlorinated biphenyls (PCBs), polychlorinated dibenzo-*p*-dioxins and -furans (PCDD/Fs), polybrominated diphenyl ethers (PBDEs), and PFASs). The problems associated with persistent chemicals including the resulting poorly reversible contamination and chemical exposures have long been known and discussed repeatedly in the literature (Stephenson, 1977;

Klöpffer, 1994; Scheringer, 1997; Persson et al., 2013; EEA, 2002; EEA, 2013). Despite this knowledge, the problems associated with poorly reversible contamination have not been adequately addressed in chemicals regulations and society continues to accrue enormous clean-up costs associated with legacy contamination. For example, the costs of the legacy of PCB contamination in the European Union have been estimated to be as high as 75.3 billion Euros between 1971 and 2018 (EEA, 2002; EEA, 2013). It is yet unknown what the costs of AFFF-related PFAS contamination globally will be, but they are also likely to be enormous. For example, the costs to clean up a small site on the Channel Island of Jersey, United Kingdom, where the drinking water for 23 households was contaminated by PFOS from the use of AFFFs for training, were between 3.7 and 30 million pounds Sterling (at 1999–2000 prices) (States of Jersey, 2004). The costs of cleaning up the contaminated site is only one of many costs associated with the contamination legacy from PFAS-containing fire-fighting foams; others include analytical costs for monitoring of PFAS concentrations, incineration of old stockpiles, clean-up of equipment contaminated by previous use, costs of developing and commercializing sustainable alternatives, costs of funding new research, health costs, legal costs, etc. Most of these costs will be borne by taxpayers, as it is challenging and often costly to identify the principal responsible party or parties in practice. Hence, early actions that lead to pollution prevention are much more cost-effective for society than late actions to clean up the pollution.

As we discuss above, the vPvB criteria as they are applied under REACH are not adequate metrics for assessing the reversibility of exposure and new approaches are needed. It has been known for some time that all PFASs which contain persistent perfluoroalkyl moieties (C_nF_{2n+1}) will ultimately degrade to form non-degradable P chemicals in the environment. Therefore, poorly reversible PFAS exposures will arise in (parts of) the environment. We argue that if poorly reversible exposure had been used as a criterion to regulate PFASs according to the precautionary principle, then PFASs would have been regulated at an earlier stage. However, instead of implementing a precautionary approach, the usual risk-based regulatory approach has been applied. Risk assessment requires a substantial amount of information to prove that there are unacceptably high risks before any action can be taken. Therefore, although high levels of PFASs were identified as early as the late 1990s near to areas where AFFFs had been used or spilled (Moody and Field, 2000), it took a further decade to conduct the overwhelming research and consultancy needed to set risk-based guidelines for levels in drinking water, and even today these guidelines continue to be refined and debated intensely.

We maintain that regulatory criteria are needed for identifying chemicals and chemical uses that lead to poorly reversible exposures. Poorly reversible exposures can occur (1) due to slow elimination kinetics in organisms or (2) due to poorly reversible environmental contamination that leads to continuous exposure. Condition (2) occurs if (a) a substance has a long environmental half-life or ultimately degrades to form substances that have long environmental half-lives (e.g. in the case of precursors to PFAAs) or (b) a substance has poorly reversible emissions (Persson et al., 2013) (e.g. if the use is considered essential). For condition (2a) there are already well-defined regulatory criteria (e.g., the P or vP criteria in the REACH regulation). Condition (1) is related to bioaccumulation, but as shown above the conventional B criterion used in existing regulation is not an adequate predictor of elimination kinetics in humans. The elimination half-life of the chemical in humans (or other target organisms of concern) could be an appropriate regulatory criterion for condition (1). To address condition (2b), new regulatory concepts must be developed that identify combinations of chemical properties and chemical uses that would limit society's ability to reduce emissions of the chemical after it had come into use. Unfortunately, society will continue to use and emit PFAS-based AFFFs in some firefighting applications for the foreseeable future because some users contest that there is a lack of alternatives that provide comparable performance. Although the toxicity of the substance will ultimately determine if the exposure is harmful, there is often a high uncertainty regarding this criterion. This can be a strong argument for not including toxicity in a precautionary regulatory approach, as is the case in the REACH vPvB assessment; poor reversibility of exposure would be a stand-alone criterion for regulation.

If society is to implement a precautionary approach to reduce the likelihood of poorly reversible exposures, “design for degradation” will need to be increasingly implemented in chemical product manufacture. “Design for degradation” denotes one of the 12 principles of Green Chemistry, namely “chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment” (Anastas and Warner, 1998). According to this reasoning, society should replace all PFAS-based fire-fighting foams with non-persistent fire-fighting products, given that they can lead to poorly reversible exposures. A recommendation to limit the production and use of PFASs due to their high persistence was also recently made in the Helsingør (Scheringer et al., 2014) and Madrid Statements (Blum et al., 2015).

Interestingly, and in parallel to our work, a report on behalf of the German Federal Environmental Agency has recently recommended hazard assessment criteria that omit the B criterion for protecting against chemical contamination of “raw water” (e.g. groundwater) used for drinking water (UBA, 2014). Instead of the REACH PBT criteria (REACH, 2007), they recommend using P, M (“mobility”, which is

dependent on soil sorption) and T (toxicity) criteria for protecting raw waters from contamination and suggest that even low levels of PMT substances in raw waters should be avoided. M provides an indication of the fraction of chemical that will reach the groundwater and thus the magnitude of exposure.

PFAS-containing fire-fighting foams in current use are often based on shorter perfluoroalkyl chain lengths, such as 6:2-fluorotelomer sulfonamide alkylbetaine (Wang et al., 2013), which will degrade in the environment and biota to form short-chain PFAAs (mostly PFHxA). There are currently few toxicological data published for PFHxA in the peer-reviewed literature and no specific drinking water guidelines have been established for this substance. Industry studies (e.g. Iwai and Hoberman, 2014; Klaunig et al., 2015) indicate that PFHxA is less toxic than PFOA and PFOS. Nevertheless, contamination of drinking water aquifers with short-chain PFAAs is likely because these substances are highly persistent, highly mobile in soils and aquifers (i.e. high solubility in water and low adsorption to organic matter) and will reside in the drinking water aquifers as long as the groundwater itself, i.e. decades to centuries (Guelfo and Higgins, 2013). Levels of short-chain PFAAs will increase in drinking water aquifers near to continuous point-source releases of PFAS-containing fire-fighting foams (e.g. military bases). If the drinking water originating from these contaminated aquifers is not effectively treated, humans will be exposed to the PFAAs and human serum levels will also increase. It is noteworthy that short-chain PFAAs fulfill the P and M criteria (M will decrease with perfluoroalkyl chain length) suggested in the German Federal Environment Agency report (UBA, 2014) discussed above and they are also highly bioavailable to humans (Gannon et al., 2011; Russell et al., 2013; Zhou et al., 2014). Long-chain PFAAs are clearly toxic (De Wit, 2015), but it is unclear if short-chain PFAAs would fulfill the T criterion in the German report due to the uncertainties in their toxicity.

Effective fire-fighting foams are needed and designing fluorine-free fire-fighting foams for rapidly extinguishing class-B fuel fires is a technical challenge. Significant innovation is required to either redesign fire extinguishing processes (i.e. functionality replacement) or develop alternative surfactants that have excellent surface activities equal or similar to that of fluorosurfactants (i.e. chemical replacement). Encouraging progress is being made. Some fluorine-free foam manufacturers have claimed that AFFFs are not necessary for effectively extinguishing all types of class-B fuel fires (Sontake and Wagh, 2014; Williams et al., 2011). A wide range of fluorine-free foams which perform well in many fire-fighting situations are already on the market (Hetzer et al., 2014). Indeed, all Swedish and Norwegian commercial airports have recently replaced PFAS-based AFFFs with fluorine-free foams because of environmental safety concerns (Norström and Viktor, 2011). Additionally, the US EPA has awarded their 2014 Designing Greener Chemicals Award to a fluorine-free fire-fighting foam (US EPA, 2014) based on a blend of hydrocarbon surfactants. Development of novel siloxane surfactants-based AFFFs is also underway and these display nearly the same performance in fire tests as PFAS-based AFFFs (Hetzer et al., 2014; Blunk et al., 2014).

In the special cases where PFAS-based foams are currently the only viable option for extinguishing certain extreme fires, extra care should be taken during use and disposal. For example, in Germany there are guidelines for responsible use (UBA, 2013), which include the use of non-fluorinated “training foams” in training activities, containment and collection of PFAS-containing fire-fighting foam residues used for fire-fighting, and appropriate treatment of collected wastes. In any substitution strategy, environmental and human health risks from exposure to chemicals in fire-fighting foams as well as clean-up costs for society have to be balanced against the technical performance of the foams in extinguishing fires and thus fire risk to human life. The eventual replacement of persistent PFASs in fire-fighting foams with degradable alternatives that achieve acceptable functionality is a strategy that is in harmony with a future sustainable society.

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Appendix A. Supplementary data

Additional information on the one-box pharmacokinetic model used to generate Fig. 2 and its parameterization. Supplementary data associated with this article can be found in the online version, at <http://dx.doi.org/10.1016/j.envint.2016.04.044>.

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